Short communication

Hydrogen/deuterium storage properties of Pd nanoparticles

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HIGHLIGHTS

► We prepared the Pd nanoparticles of 10 nm by dealloying method.
► They can absorb/desorb hydrogen or deuterium quickly at room temperature.
► There is no apparent isotope effect on the sorption kinetics of Pd nanoparticles.
► The diffusion coefficients of hydrogen and deuterium in Pd are similar.
► Deuterium isotherm shows higher plateau pressure and narrower gap than hydrogen.

GRAPHICAL ABSTRACT
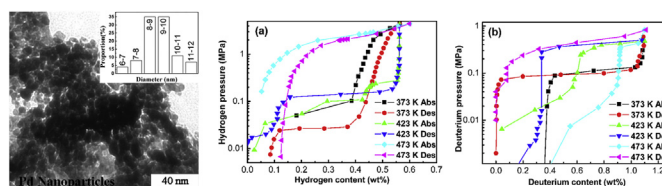
ARTICLE INFO

ABSTRACT

The Pd nanoparticles of 10 nm have been prepared by dealloying method. They can absorb/desorb hydrogen or deuterium completely in a few seconds at room temperature. There is no apparent isotope effect on the sorption kinetics. The activation energies of hydrogen and deuterium absorption are 23.2 and 23.7 kJmol^{-1}, respectively. The diffusion coefficients of hydrogen and deuterium in the Pd nanoparticles are similar at 423 K. However, the deuterium isotherm shows higher plateau pressure and narrower gap than the hydrogen isotherm at the same temperature. When the temperature increases to 473 K, no phase transformation can be detected for both hydrogen and deuterium. The particle size and structure effects on the hydrogen/deuterium sorption process are discussed.

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1. Introduction

Hydrogen energy is becoming increasingly important due to the limited reserves and related environment pollution of the conventional fossil fuel. It has been considered as a promising energy carrier in future energy systems, however, the widespread use of hydrogen is still challenged by its storage technology, especially for the applications in vehicles powered by fuel cells and in hydrogen fuelled internal combustion engines. In order to satisfy the commercial application requirements, hydrogen storage materials should follow such criteria: safety, high capacity and mild operation conditions [1]. Recently, a series of materials such as carbon [2], metal-organic frameworks (MOFs) [3], metal hydrides [4], alanates [5], and amides [6] have been developed for hydrogen storage. However, practical application of these materials is still limited due to their poor sorption kinetics [7,8]. Some researches have suggested that the poor sorption kinetics was associated with high

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activation energy for the dissociation of H_2 molecule on the surface of these hydrogen storage materials [9,10]. Based on this result, some transition metals were added as catalysts to improve the dissociation of H_2 molecule. Among them, Pd was considered as one of the most effective catalysts to improve the sorption kinetics [11,12].

It is known that the activation process of Pd includes two parts. In the first step, H_2 molecules are dissociated into hydrogen atoms on the Pd surface. In the second step, hydrogen atoms transport into the hydrogen storage materials from the Pd catalyst. The two steps involve the dissociation of H_2 molecule and the diffusion of hydrogen atom, respectively. However, how the two steps affect the sorption is still ambiguous. Although there are a few of investigations on the hydrogen storage properties of Pd and Pd doped materials [13–21], the hydrogen sorption properties of Pd nanoparticles are deficient. When the particle size decreases to nanoscale, the properties of Pd may be changed. Therefore, it is necessary to clarify the hydrogen storage properties of Pd nanoparticles. In this work, we intend to investigate the storage kinetics, activation energy and diffusion coefficient of hydrogen/deuterium sorption of Pd nanoparticles, and discuss the isotope effect and the particle size effect on hydrogen storage properties of Pd nanoparticles.

2. Experimental

The Al_6Pd ingot was prepared from bulk Pd and Al (purities >99.9 wt.%) by arc melting in an argon gas atmosphere. The arc-melted ingot was flipped over and remelted four times to get a homogeneous composition. Then, the alloy was crushed into microsize and dissolved in an aqueous 20 wt. % sodium hydroxide solution to remove the Al element. After dealloying, the nanoparticles were separated from the dealloying solution and repeatedly washed with deionized water until the pH of the washing water was neutral. The nanoparticles were finally washed by ethanol and dried at 333 K in vacuum for 6 h.

The structural analysis of the nanoparticles was carried out by X-ray diffraction (XRD) using an automated Rigaku X-ray diffractometer with monochromatic Cu Kα radiation. The size distribution and morphology of these nanoparticles were observed by transmission electron microscopy (TEM) using JEOL-JSM-2100F at an accelerating voltage of 200 kV.

The hydrogen absorption and desorption properties of the nanoparticles were evaluated using a Sieverts-type apparatus. The volume of the reactor chamber was about 60 ml, and the measurement error was less than 5%. The sample about 0.3 g was pressurized to a disc shape (10 mm in diameter and about 0.5 mm in thickness) under 120 MPa in order to obtain the diffusion coefficient in each measurement. After the sample was put into the Sieverts reactor, the system was evacuated to 10^{-3} Pa. Then, the sample was heated and kept at certain temperature. To measure the absorption kinetic curves, a hydrogen pressure of 0.3 MPa was provided to make the sample absorb hydrogen. The desorption kinetics was obtained at various temperatures with an initial pressure of about 1 Pa by evacuating the system. A conventional pressure-volume−temperature technique was used to get the hydrogen sorption curves at each temperature. The pressure−composition−temperature (P−C−T) curves of the sample were measured at 373, 423 and 473 K by increasing/decreasing the hydrogen pressure gradually. Once the change of hydrogen pressure was less than 10 Pa per second, the hydrogen absorption or desorption process at certain pressure during the P−C−T measurement was considered as reaching the equilibrium. Deuterium was used to substitute hydrogen to obtain the deuterium storage properties of Pd nanoparticles in order to investigate the isotope effect.

3. Results and discussion

Fig. 1 shows the XRD result of the Pd nanoparticles. The peaks can be attributed to (111), (200), and (220) planes of Pd (JCPDS 46-1043, space group: Fm3m). No other phases can be detected in the obtained sample. Determined by the Scherrer equation, the crystalline size of Pd nanoparticles is about 6 nm. The morphology and microstructure of the sample was further investigated by electron microscopy. From the TEM image in Fig. 2a, it can be seen that the Pd nanoparticles exhibit a narrow particle size distribution from 6 to 12 nm with an average particle size of about 10 nm Fig. 2b displays the high resolution TEM image of one Pd nanoparticle. The crystalline size of the nanoparticle is about 3−6 nm, similar with the results derived from the XRD result.

Fig. 3 presents the absorption curves of the Pd nanoparticles under an initial pressure of 0.3 MPa of hydrogen at different temperatures. The sample can absorb 0.53 wt. % hydrogen in 1 min at 300 K, showing superior hydrogen absorption kinetics. As the temperature increases, the absorption rate rises. At 373 K, the Pd nanoparticles absorb hydrogen completely to form $PdH_{0.6}$ in a few seconds. Fig. 4 displays the hydrogen desorption of Pd nanoparticles at 323, 348 and 373 K under an initial pressure of 1 Pa hydrogen. The desorption can be completed at these temperatures in a few seconds. It is well known that the hydrogen absorption process of Pd includes four parts: adsorption of hydrogen molecule on the metal surface, dissociation of hydrogen molecule to form hydrogen atom, diffusion of hydrogen atom and nucleation of hydride. In the desorption process, the reversed steps takes place. It is also known that smaller particle and crystalline sizes facilitate the hydrogen sorption because of the reduced diffusion distance. In our experiment, the particle and crystalline sizes are confined to several nanometers. Therefore, the obtained sample shows excellent sorption kinetics.

The activation energy of sorption is estimated by combining the Johnson−Mehl−Avrami equation with the Arrhenius equation after fitting the experimental data at different temperatures. The rate constant k is determined by following equation:

$$\ln[-\ln(1-f)] = \eta \ln k + \eta \ln t \tag{1}$$

where f is the growing phase fraction, t is absorption time and η is the reaction order. A plot of $\ln[-\ln(1-f)]$ versus $\ln t$ yields η and $\eta \ln k$ when $t = 1$. Then the temperature dependence of k can be correlated by the Arrhenius equation:
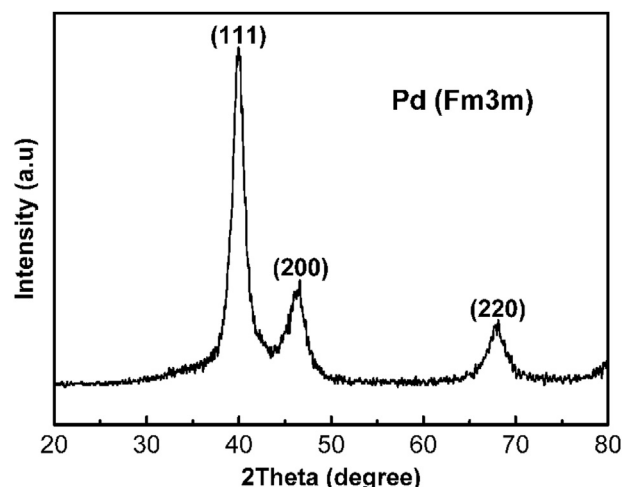

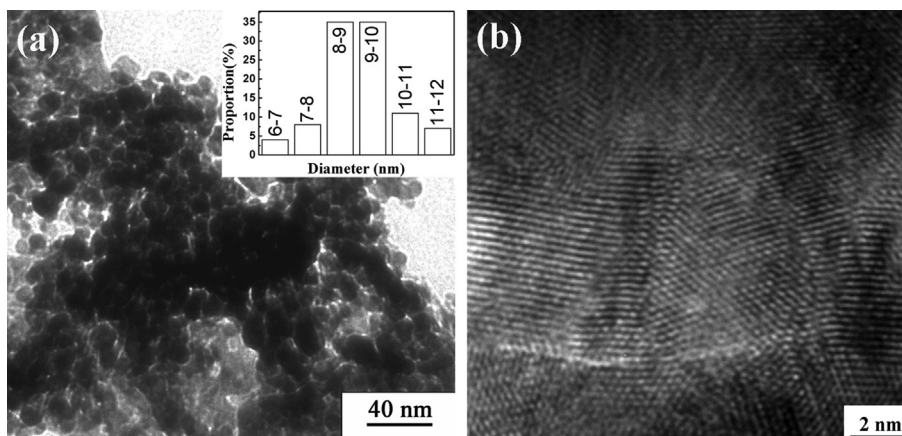**Fig. 1.** XRD pattern of the Pd nanoparticles.

Fig. 2. TEM image of the Pd nanoparticles (a), and the high resolution TEM image of one Pd nanoparticle (b).

$$k = A \bullet \exp(-E_a/RT) \qquad (2)$$

where A is a temperature-independent coefficient, E_a is the activation energy, R is the gas constant and T is the absolute temperature. Determined from Eq. (1), the $\ln k$ and η of hydrogen absorption/desorption is obtained, as listed in Table 1. All the values of η at different temperatures are close to 1, which suggests that an instantaneous nucleation formation followed by the H atom diffusion during both the absorption and desorption process. From the results of plotting $\ln k$ versus $1000\,T^{-1}$, as indicated in Fig. 5, the activation energies of the hydrogen absorption and desorption of the Pd nanoparticles are 23.2 and 25.1 kJ mol^{-1}.

In order to investigate the isotope effect, the hydrogen is changed to deuterium. Fig. 6 presents the deuterium absorption curves under the same conditions as those of hydrogen. The absorption rates are also high at 300, 323 and 373 K. It takes a few seconds for Pd nanoparticles to absorb deuterium completely. The desorption of deuterium is measured under an initial pressure of 1 Pa deuterium directly after the absorption. From Fig. 7, it can be seen that the desorption can be finished in a few seconds at 300, 348 and 373 K. However, the deuterium absorption and desorption rate are lower than those of hydrogen at the lowest temperature. When the temperature increases, there is no difference in sorption rate between hydrogen and deuterium. Determined from the same equations as discussed above, the $\ln k$ and η of absorption and

desorption are obtained, as listed in Table 2. The plots of $\ln k$ versus $1000\,T^{-1}$ are shown in Fig. 8. The activation energies of the absorption and desorption of deuterium are 23.7 and 25.8 kJ mol^{-1}, respectively.

During the dissociation of hydrogen molecule by Pd, σ electron of hydrogen donates to a vacant metal d orbital first. Then the bond is stabilized by back-donation of electrons from the filled d orbital to the anti-bonding orbital (σ*) of the bond of H$_2$. Increasing the back-donation to σ* facilitates the break of H–H bond and the formation of Pd–H bond [22]. After that, the Pd–H transfers hydrogen atoms to bulk phase. The electron orbital of deuterium is the same as that of hydrogen. Therefore, there should be no difference in the dissociation of hydrogen and deuterium on the surface of Pd. The atom radius of deuterium is larger than that of hydrogen, which may induce higher diffusion activation energy of deuterium. However, the sorption activation energy of deuterium is almost the same as that of the hydrogen, as presented in Tables 1 and 2. These results suggest that the diffusion energies of hydrogen/deuterium in the Pd nanoparticles are low. The probable reason is that the large amount of grain boundaries and small particle size of the Pd nanoparticles accelerate the diffusion. In addition, the lattices of Pd and PdH$_{0.6}$ are both the face-centered structure with the same space group of Fm3m. Therefore, the activation energy is low during the hydrogen sorption process. From these results, it can be concluded that the dissociation energy
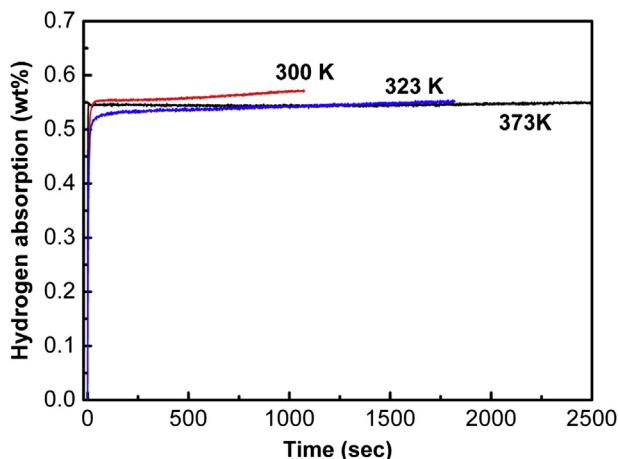

Fig. 3. Hydrogen absorption curves of Pd nanoparticles at different temperatures under an initial pressure of 0.3 MPa of hydrogen.
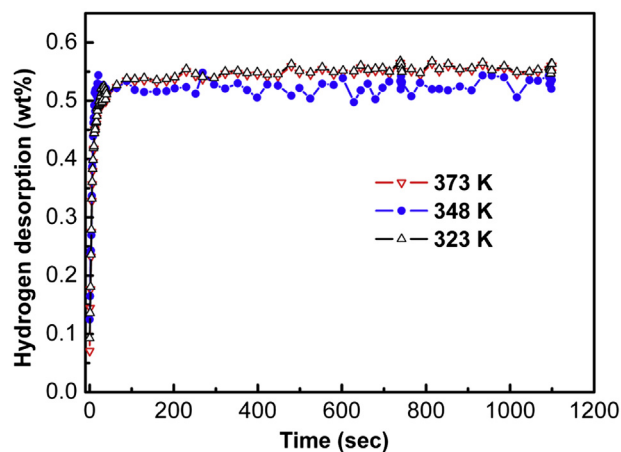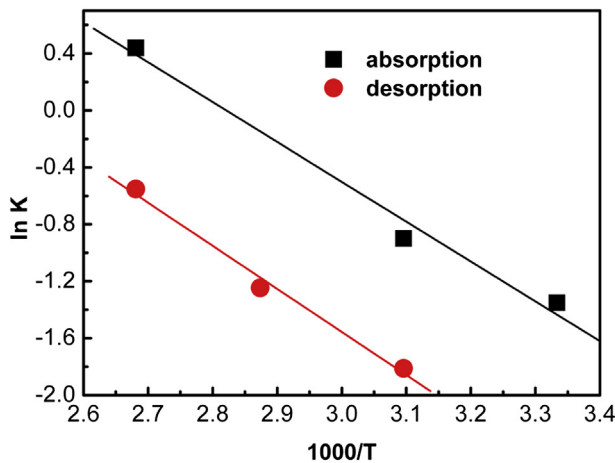

Fig. 4. Hydrogen desorption curves of PdH$_{0.6}$ at different temperatures under an initial pressure of 1 Pa of hydrogen.

	Absorption			Desorption		
	373 K	323 K	300 K	373 K	348 K	323 K
ln k	0.44	−0.90	−1.35	−0.55	−1.25	−1.81
η	0.68	0.83	0.75	0.96	0.79	0.90
E_a	23.2 kJ mol^{-1}			25.1 kJ mol^{-1}		

Fig. 5. Plots of ln k versus 1000 T^{-1} for hydrogen absorption/desorption at different temperatures.

Fig. 7. Deuterium desorption curves of PdD$_{0.6}$ at different temperatures under an initial pressure of 1 Pa of deuterium.

	Absorption			Desorption		
	373 K	323 K	300 K	373 K	348 K	323 K
ln k	−1.17	−2.30	−3.06	−1.65	−2.30	−2.95
η	0.66	1.05	0.55	1.09	0.98	0.66
E_a	23.7 kJ mol^{-1}			25.8 kJ mol^{-1}		

is the dominant factor in the hydrogen sorption process of Pd nanoparticles. Du et al. also suggested that the dissociation energy of H$_2$ on Pd atom surface was larger than the diffusion energy of H atom [9].

PCT curves for hydrogen in Pd nanoparticles at different temperatures are presented in Fig. 9a. At 373 K, the isotherm shows three distinct regions: the α phase at low hydrogen concentration, the (α + β) phase that masks the miscibility gap and the β phase at high pressure. The plateau pressures for the hydrogen absorption and desorption are 0.073 and 0.026 MPa, respectively. As the temperature increases, the miscibility gap becomes narrow and the hydrogen concentration in α phase enhances significantly. At 423 K, the maximum hydrogen concentration in α phase is about 0.5 wt.% and the plateau pressures are 0.026 and 0.016 MPa for absorption

and desorption, respectively. There is no phase change when the temperature reaches 473 K. Some former researches suggested that no phase transformation happened when the Pd particle size was decreased to a certain region [23]. It could be explained by the occupation of hydrogen atoms at the subsurface sites of Pd nanoparticles. The particle and crystalline size of the Pd nanoparticles in this work are so small that the proportion of subsurface sites increases obviously. Therefore, there is only α phase at 473 K. Although the dislocation formation is difficult for small clusters, the pressure hysteresis still exists at all temperatures.

Deuterium isotherms show the similar characters as hydrogen. However, the miscibility gaps of deuterium are narrower than those of hydrogen at the same temperature. This suggests that the deuterium atoms are inclined to occupy the subsurface sites rather

Fig. 6. Deuterium absorption curves of Pd nanoparticles at different temperatures under an initial pressure of 0.3 MPa bar of deuterium.
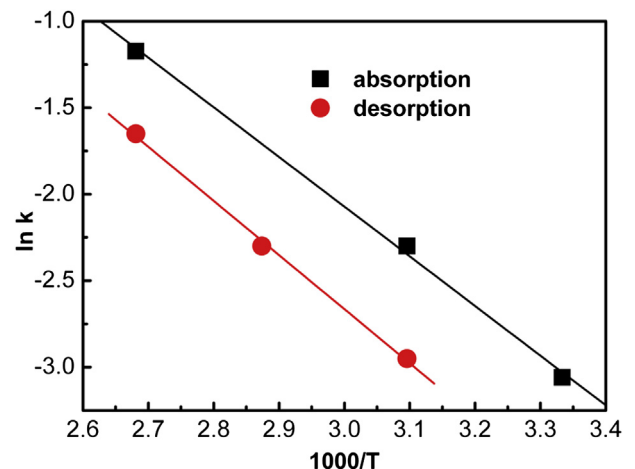

Fig. 8. Plots of ln k versus 1000 T^{-1} for deuterium absorption/desorption at different temperatures.
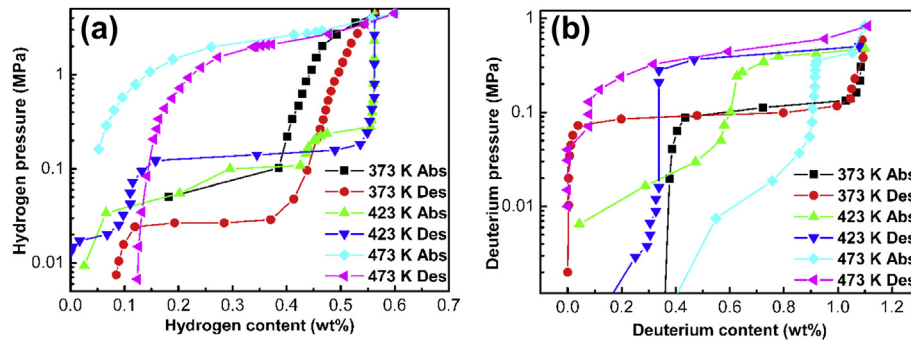
Fig. 9. PCT isotherms of hydrogen (a) and deuterium (b) at different temperatures.
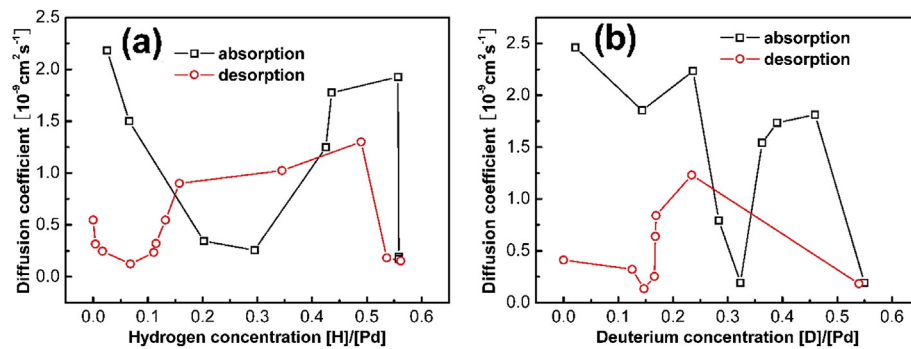

Fig. 10. Diffusion coefficient of hydrogen (a) and deuterium (b) in the Pd nanoparticles at 423 K.

than the interior sites. In addition, the plateau pressures of deuterium are higher than those of hydrogen at 373 and 423 K. The plateau pressures are 0.1 and 0.09 MPa for absorption and desorption at 373 K, respectively. When the temperature increases to 423 K, the absorption and desorption plateau pressures become 0.48 and 0.43 MPa, respectively. It is interesting that the pressure hysteresis shrinks because of the isotope effect.

During the PCT isotherm measurements, $P(t)$ which follows an exponential behavior can be given by the following equation:

$$P(t) = P_0 + (P_{eq} - P_0)[1 - \exp(\tau t)] \tag{3}$$

where P_0 is the initial pressure, P_{eq} is the equilibrium pressure, t is the time and τ is the temperature dependent time constant. Supposed that the samples in the measurements are cylindrical geometry with a constant surface concentration boundary condition, the diffusion coefficient D could be determined by the following equation according to the Fick's second law:

$$\tau = \left[(\pi/a)^2 + \left(2.405/R \right)^2 \right] D \tag{4}$$

where a is the thickness of the sample and R is the radius of sample [13]. From Eqs. (3) and (4), the diffusion coefficients D for hydrogen and deuterium absorption and desorption at 423 K are obtained, as indicated in Fig.10a and b. It is clearly shown that there is no apparent difference in diffusion coefficient between hydrogen and deuterium. These results are in agreement with the kinetics analysis as discussed above. In α phase, the diffusion coefficient decreases as the hydrogen and deuterium concentration increases with the increasing hydrogen/deuterium content. When the hydrogen and deuterium concentration reach the miscibility gap, the diffusion coefficient increases. After the α phase transforms to β phase completely with increasing pressure, the diffusion coefficient

decreases again. For the desorption process, the diffusion coefficient is the biggest during the phase transformation.

4. Conclusions

Pd nanoparticles with particle size of 10 nm and crystallite size of 6 nm show superior hydrogen/deuterium storage kinetics. They can absorb/desorb hydrogen or deuterium completely in a few seconds at room temperature. There is no apparent isotope effect on the kinetics. The activation energy of deuterium sorption is almost the same as that of hydrogen. The diffusion energy is minor and the dissociation energy is the dominant factor in the hydrogen sorption process of Pd nanoparticles. In addition, the diffusion coefficients of hydrogen and deuterium in the Pd nanoparticles are similar at 423 K. However, the deuterium isotherm shows higher plateau pressure and narrower gap than the hydrogen isotherm at the same temperature. There is no phase transformation at 473 K. Deuterium isotherms show the similar characters as hydrogen except that the plateau pressure is higher and the miscibility gap is narrower.

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